

Interpenetrating Polymer Networks of Cellulose Nitrate and Castor Oil Based Polyurethanes—Development and Characterization

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Synopsis

Semi-interpenetrating polymer networks of cellulose nitrate and castor oil based polyurethanes have been prepared by using excess diisocyanate for the crosslinking process. Semi-IPNs with 30% cellulose nitrate showed some degree of miscibility. Enhanced miscibility was observed by the partial replacement of cellulose nitrate with poly(vinyl chloride-co-vinyl acetate). The ternary IPNs of poly(vinyl chloride-co-vinyl acetate), cellulose nitrate, and polyurethanes showed increased tensile strength and decreased flammability than those based on cellulose nitrate and polyurethanes alone.

INTRODUCTION

Cellulose nitrate is a widely used cellulose derivative in the protective and decorative lacquer coatings applications. These coatings, however, are not very satisfactory in their thermal stability and low temperature flexibility. Flexibility can either be improved with plasticizers such as castor oil and resins or by combining cellulose nitrate with suitable polymers such as polyurethanes derived from castor oil. Both cellulose nitrate and polyurethanes require complete modification in order to improve their flame resistance. An attempt has been made to improve the shortcomings of cellulose nitrate by combining it with castor oil based polyurethanes and poly(vinyl chloride-co-vinyl acetate) (Vc-VAc).

Mechanical blending is the traditional way of combining two or more polymers to provide products with superior chemical and physical properties. Blended polymers, however, often experience phase separation due to the lack of suitable bonding forces between the two polymer phases.¹ In the present investigation, combination of cellulose nitrate with polyurethanes and poly(vinyl chloride-co-vinyl acetate) has been effected by interpenetrating polymerization—a mode of blending two or more polymers to produce a mixture in which phase separation is not as extensive as it would be otherwise.

Interpenetrating polymer networks (IPNs) are more or less intimate mixture of two or more distinct crosslinked polymers mutually held together by per-

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manent entanglements containing essentially no covalent bonds or grafts between them. It is a mixture of two polymers crosslinked or reacted in the presence of each other.²⁻⁵ If both polymers are crosslinked, it is called a full IPN, while if one is crosslinked and the other is linear it is called a semi-IPN.⁶ The interpenetrated and entangled networks can increase the phase stability and therefore enhance the properties of the resulting material.

IPNs of castor oil based polyurethanes with divinyl benzene-styrene copolymer and poly(methyl methacrylate) have been reported.⁷⁻¹² Extensive studies have recently been made on the compatibility of IPNs by using stable nitroxide spin probes.^{13,14} In this present work ternary semi-IPNs of cellulose nitrate, poly(vinyl chloride-co-vinyl acetate) and castor oil based polyurethanes have been developed and characterized.

EXPERIMENTAL

Commercial grade cellulose nitrate (NC) and vinyl chloride-vinyl acetate (Vc-VAc) copolymer, reprecipitated were used after drying under vacuum for two days. The GPC data of these two are given in Table I. Castor oil was used after drying under vacuum at 100°C for 1 h. Toluene diisocyanate and hexamethylene diisocyanate (specific gravities 1.225 and 1.05, respectively) were used as such.

SYNTHESIS OF IPNs

Dried nitrocellulose was dissolved in distilled methyl ethyl ketone. Calculated amount of weighed castor oil was added into the nitrocellulose solution followed by a few drops of dibutyltindilaurate. After stirring for 5 min calculated amount of diisocyanate was added in drops and the entire solution was stirred at 60°C for 4 h under nitrogen atmosphere. The resultant solution was cast as a film. In preparing the ternary IPNs, both nitrocellulose and the copolymer were dissolved in methyl ethyl ketone, and the above procedure was adopted. Films with different compositions were prepared.

CHARACTERIZATION

SEM

The morphology of semi-IPNs thus prepared was studied by using a scanning electron microscope. Samples of very thin sections were prepared from the

TABLE I
GPC Data for Nitrocellulose and Vinyl Chloride-Vinyl Acetate Copolymer

Material	M_n	M_w	M_v	Z_{av}	Polydispersity	Intrinsic viscosity
Nitrocellulose	2.7×10^4	7.6×10^4	7.6×10^4	3.8×10^6	2.8	0.0766
Copolymer	3.33×10^4	6.57×10^4	6.56×10^4	3.23×10^5	1.973	0.0657

films and mounted on an aluminum stud. They were gold coated in an Edwards sputter coating unit and scanned in a Philips Scanning electron microscope.

Tensile Strength

These measurements were carried out according to ASTM D638 (1977). The specimens were prepared from the sample by using a dumbbell die of width 0.4 cm and length 2.2 cm in the narrow portion. Thickness of the specimens was measured after conditioning at 25 + 2°C for 4 h. Tensile strength of each specimen was then measured in an Instron Universal Testing Machine Model 1112. The rate of separation of the power actuated upper grip was maintained at 100 mm/min.

Limiting Oxygen Index

The flammability characteristics of the semi-IPNs were determined in terms of their limiting oxygen index. The ASTM D 2863 oxygen index test determines the relative flammability of plastics by measuring the minimum amount of oxygen, in a mixture of oxygen and nitrogen, which is required to support the combustion. The relation used to determine LOI is as follows:

$$\text{LOI} = \frac{\text{volume fraction of O}_2}{\text{volume fraction of O}_2 + \text{volume fraction of N}_2} \times 100$$

Samples of 50 mm height, 5 mm thickness, and 20 mm width were used to determine LOI. Each sample was clamped vertically over a stand in a glass cylinder and allowed to burn in a controlled stream of nitrogen and oxygen atmosphere.

DSC

Glass transition temperatures for some selected IPNs were found out by a Perkin-Elmer 7 series thermal analysis system. A sample of about 30 mg was weighed with the microbalance AD-4 and encapsulated in an Aluminium crucible. Then the sample was heated at the rate of 10 K/min from -60°C to 250°C.

RESULTS AND DISCUSSION

Morphology

The morphology of various semi-IPNs of nitrocellulose, vinyl chloride-vinyl acetate copolymer and polyurethanes are shown in the SEM photographs. IPNs prepared with 25 and 40% nitrocellulose content were found to be immiscible whereas those with 30% nitrocellulose content showed partial miscibility (Fig. 1). But the miscibility is enhanced when part of the nitrocellulose is replaced with the copolymer. This enhanced miscibility is evident from the more homogeneous SEM photographs (Figs. 2-5). The 40/60 composition with 10% NC and 30% Vc-VAc copolymer shows almost a single phase morphology. This enhancement in phase mixing may be due to a compatibilizing action of the copolymer between the polyurethanes and nitrocellulose.

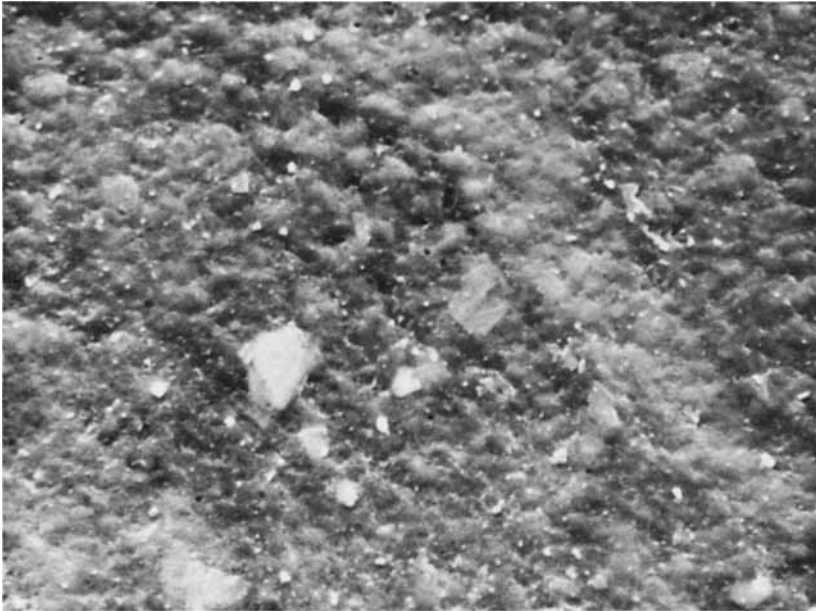


Fig. 1. SEM Micrograph of Semi IPN Composition NC/PU: 30/70 \times 1250.

Tensile Strength

Semi-IPNs of nitrocellulose prepared from TDI based polyurethanes were brittle. This brittleness may be due to the rigidity imparted by the aromatic

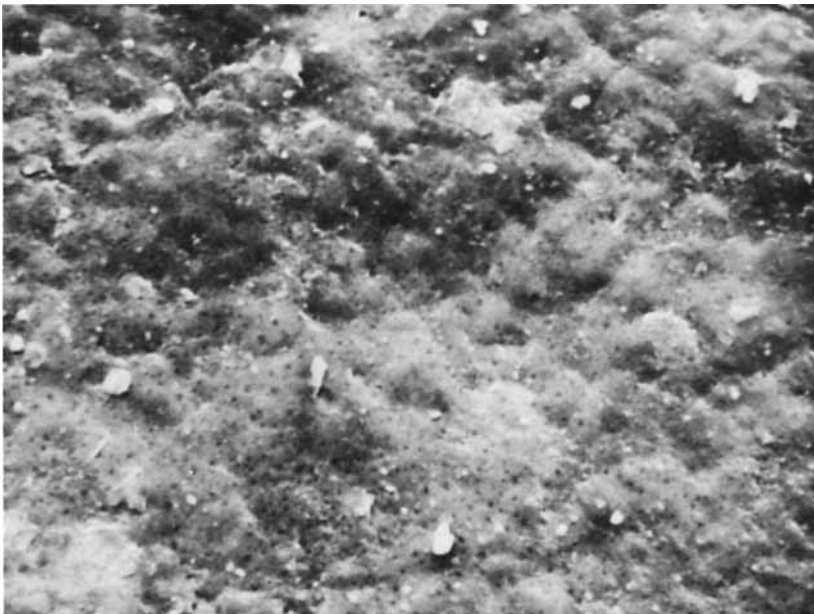


Fig. 2. NC/PU/Vc-VAc Copolymer 7.5/70/22.5 \times 1250.

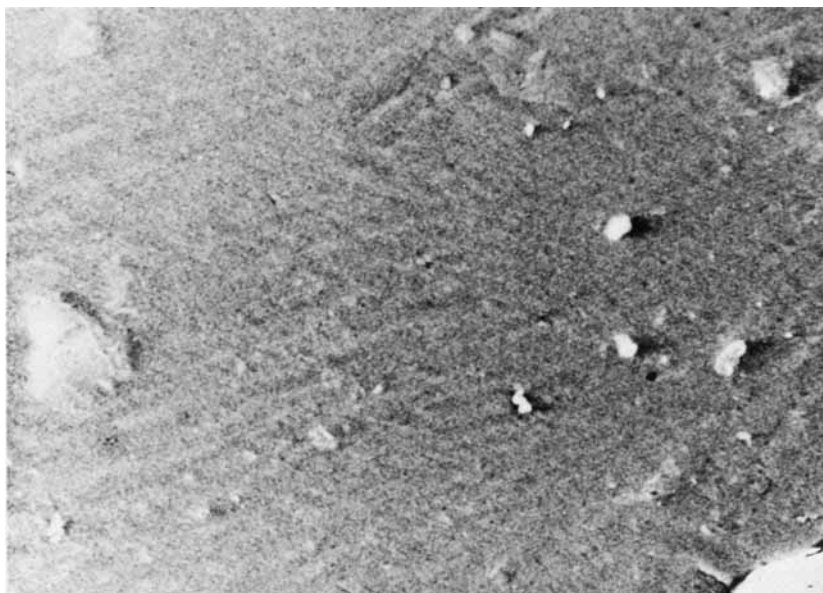


Fig. 3. NC/PU/Vc-VAc Copolymer 15/70/15 \times 1250.

diisocyanate to the already brittle nitrocellulose. But IPNs based on HMDI were flexible and their tensile strength values are given in Table II. For IPNs containing 25 and 30% nitrocellulose, tensile strength increases with NCO/OH ratio, whereas those based on 40% nitrocellulose show a reverse in trend. Because of the increase in crosslink density, the 25 and 30% nitrocelluloses

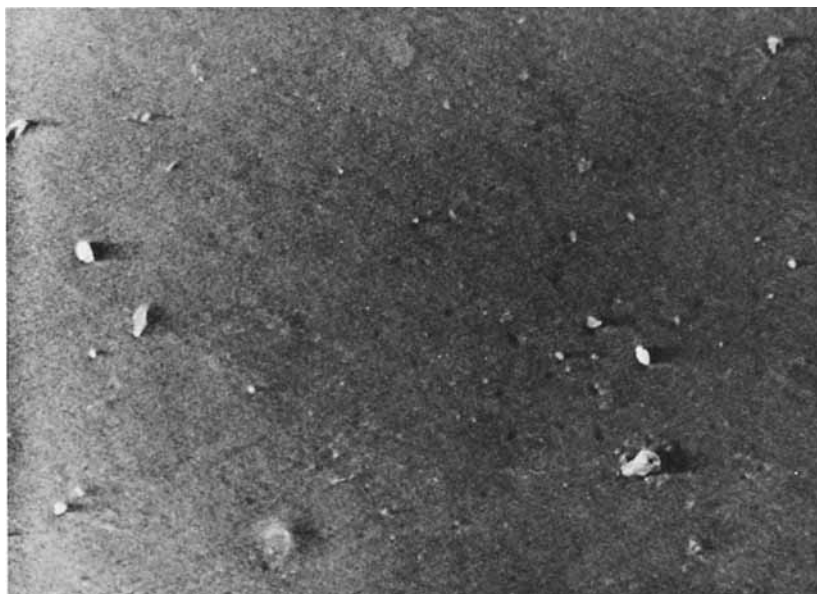


Fig. 4. NC/PU/Vc-VAc Copolymer 10/60/30 \times 1250.



Fig. 5. NC/PU/Vc-VAc Copolymer 20/60/20 \times 1250.

show an increase in tensile strength with NCO/OH ratio. In 40% nitrocellulose, though the tensile strength values are higher than those based on 25 and 30%, the tensile strength values decrease with NCO/OH ratio because, increase in crosslink density enhances the rate of phase separation, thereby reducing the phase continuity, which results in decrease in the tensile strength.

It is, however, interesting to note that, IPNs of nitrocellulose and polyurethanes with the vinyl chloride–vinyl acetate copolymer show an increase in

TABLE II
Tensile Strength of NC-Polyurethane Semi-IPNs

Composition	NCO/OH ratio	Tensile strength (kg/cm ²)	Elongation at break (%)
25% NC	1.1	32.66	200
	1.3	38.11	123
	1.5	47.85	110
75% urethane	1.7	88.49	95
30% NC	1.1	48.2	140
	1.3	52.7	125
	1.5	68.68	123
70% urethane	1.7	71.87	118
40% NC	1.1	133.08	78
	1.3	101.79	78
60% urethane	1.5	98.66	77
	1.7	94	70

TABLE III
Effect of Vinyl Chloride-VAc Copolymer on Tensile Strength

Composition	NCO/OH ratio	Tensile strength (kg/cm ²)	Elongation at break (%)
15% NC	1.1	57.34	60.22
70% urethane	1.3	60.96	57.31
15% Vc-VAc Copolymer	1.5	124.88	75
	1.7	318.81	125.56
20% NC	1.1	95.59	61.04
60% polyurethane	1.3	245.74	91.63
20% Vc-VAc Copolymer	1.5	263.31	89.22
	1.7	292.34	79.22

tensile strength with NCO/OH ratio (Table III). This indicates that, the compatibility of the 40/60 composition is enhanced when part of the nitrocellulose is replaced with the copolymer. This is also evident from the SEM micrographs. The compatibility between nitrocellulose and polyurethane is increased considerably by the compatibilizer action of the copolymer.

Flammability

Flammability of a polymer is characterized by the response of the polymer to a specific ignition stimulus. The limiting oxygen index (LOI) values, a measure of relative flammability, of the IPNs are given in Table IV. The low LOI of nitrocellulose and polyurethane semi-IPNs indicate their poor flame resistance. The relative increase in LOI values with the copolymer indicate the improvement in flame resistance. This is a direct consequence of the fact that the halogen radicals act as radical scavengers on the vapour phase and therefore inhibit combustion.

DSC

Glass transition temperatures for some selected IPNs are given in Table V. All the IPNs tested have shown single transition temperatures (T_g) for the

TABLE IV
Limiting Oxygen Index of Semi-IPNs

Composition			LOI
% NC	% PU	% Vc-VAc copolymer	
25	75	—	12
30	70	—	12
15	70	15	15
20	60	20	20
10	60	30	23

TABLE V
 T_g Values of Semi IPNs

	Composition			NCO/OH	Diisocyanate	T_g °C
	% NC	% PU	% Vc-VAc copolymer			
A	30	70	—	1.1	HMDI	-26.5
B	30	70	—	1.3	HMDI	-23.9
C	30	70	—	1.5	HMDI	-18.9
D	15	70	15	1.5	HMDI	-24.8
E	7.5	70	22.5	1.5	HMDI	-28.3
F	—	75	25	1.5	TDI	-6.8

temperature range of -60°C to 250°C (Figure 6). Further, it is evident from the results that T_g increases with increase in crosslink density (i.e., increase with NCO/OH ratio). In the ternary semi-IPNs based on HMDI, when nitrocellulose is replaced by the copolymer, T_g decreases with increasing copolymer content. When toluene diisocyanate is used for copolymer-polyurethane IPNs, T_g has increased considerably because of the stiffening effect of the aromatic ring. The exothermic peak in the range 150 – 220°C shows the oxidation of cellulose nitrate.

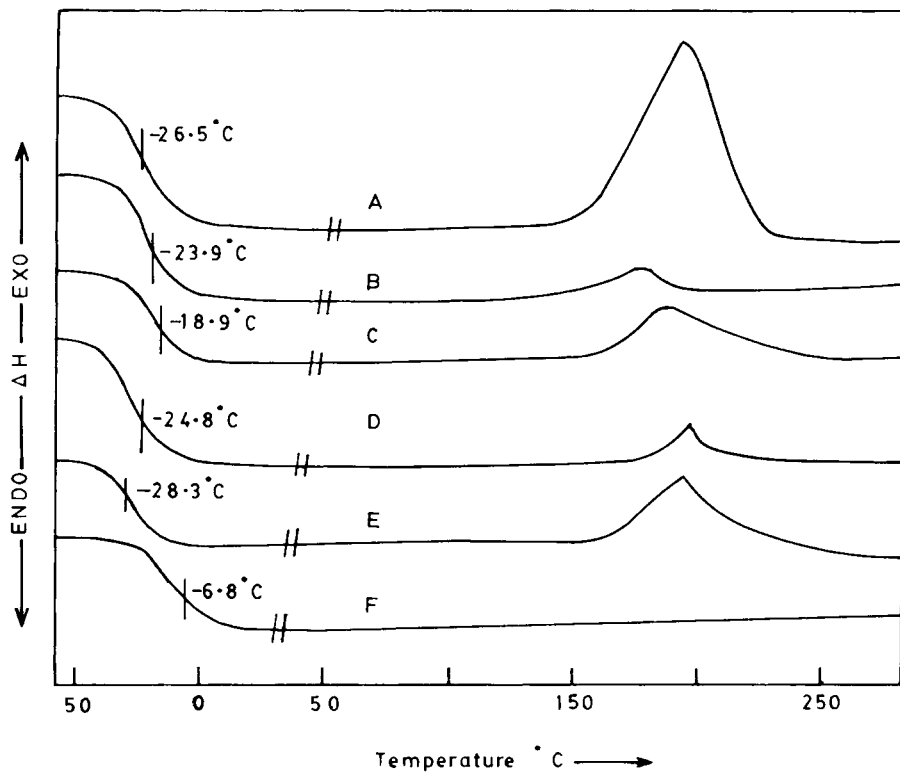


Fig. 6. DSC Curves of ternary semi IPNs.

CONCLUSION

Semi-IPNs of nitrocellulose and castor oil based polyurethanes were found to be compatible at 30% nitrocellulose content. Compatibility was further enhanced when nitrocellulose was replaced partly by vinyl chloride-vinyl acetate copolymer. Improved mechanical properties and relative improvement in flame resistance were observed for ternary IPNs with the copolymer.

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Received March 19, 1990

Accepted April 11, 1990